

CLAIMS:

- 5 1. A process for dyeing leather by simultaneous application of acidic and basic dyestuffs, which comprises treating the leather at above pH 7.5 with aqueous floats comprising solutions of combinations of these oppositely charged dyestuffs
10 in the presence of alkalis.
2. The process according to claim 1 wherein the dyeing is carried out at between pH 8 and pH 10.
- 15 3. The process according to claim 1 or 2 wherein the dyeing float further comprises alkali-stable dyeing auxiliaries and/or fatstuffs.
4. The process according to claims 1 to 3 wherein the
20 dyeing is carried out with heating.
5. The process according to claims 1 to 4 wherein chrome- and mineral-tanned leathers are used.

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2638236

Docket No.:

HOE 76/F 203

Date: August 24, 1976

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Process for dyeing leather by simultaneous application
of acidic and basic dyestuffs

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Leather is dyed using predominantly acidic or basic
leather dyestuffs, the choice of which depends on the
particular leather species, the type of tanning which
has been performed, the charge character of the leather
10 to be dyed and the desired requirements for the leather
article manufactured later.

Acidic dyestuffs dye and fix particularly efficiently,
in an aqueous medium, on cationically charged leathers,
15 resulting for example from the most common method of
tanning with chromium III salts. Basic leather
dyestuffs have less affinity for this species of
leather, since they carry the same charge as the
leather and therefore do not go onto the leather from
20 aqueous baths.

Anionically charged leathers, for example leathers
tanned or retanned with vegetable or synthetic tanning
agents, by contrast, are dyed by basic dyestuffs, which
25 exhaust readily from aqueous baths, in highly saturated
shades, whereas anionic dyestuffs color the substrate
too deeply and usually do not produce saturated-shade
dyeings.

30 To increase the depth of shade in the field of leather
dyeing in general, the commercial practice has hitherto
been to apply a bottom dyeing on the various particular

leather species with the above-described dyestuff classes acknowledged as suitable for this purpose, and thereafter to add a top dyeing with the oppositely charged other group of dyestuffs. However, this usually
5 requires a change of bath, since the oppositely charged dyestuffs would otherwise mutually flocculate in the aqueous medium used and this precipitation would then form a smeary deposit on the flesh side of the leather. Although if particular care is taken with the dyeing,
10 the oppositely charged dyestuff can also be added to the main dyebath at the end of the dyeing operation, viz., when the bottom dyestuff has already gone on fully or almost fully.

15 The sandwich process, as it is known, is one version of the change-about dyeing process described above. In the sandwich process, the main dyeing is initially performed with just half the quantity of the suitable dyestuff, then the bath is changed, and an inter-
20 dyeing is carried out with the oppositely charged group of dyestuffs. Thereafter, the second part of the main dyeing with the first dyestuff is carried out either in a fresh bath or in the well-exhausted inter-bath.

25 The aforementioned dyeing methods from an aqueous medium all have the purpose to produce fuller and deeper dyeings, i.e., to fix more dyestuff on the leather than the equivalent polar groups of the leather are able to take up on their own. However, it has
30 hitherto not been possible to dye basic and acidic dyestuffs simultaneously from an aqueous float onto leather in one main dyeing step, since the oppositely charged dyestuffs cause each other to precipitate.

35 It has only been comparatively recently that a dyeing process was launched whereby simultaneous basic-acidic dyeing in one operation became possible. In this process, known as cold dyeing without float, the pulverulent, undissolved basic and acidic dyestuffs are

milled together at room temperature into the leather without water in a dyeing drum. The residual water present in the leather from preceding operations is expressed out of the leather interior by the milling
5 process, which is much more intensive than working with long floats; dissolves some of the pulverulent dyestuff mixture; and forms a highly concentrated dyestuff solution with high penetration pressure and good leveling capacity. Owing to the supersaturated
10 solution, which is not hot, the dissociation of the dyestuffs is greatly suppressed in this method, and so the two groups of dyestuff do not precipitate despite their opposite charges. However, comparatively large quantities of hot water have to be added at the end of
15 the dyeing in order that the dyestuffs may become fixed to the leather fiber.

The most important disadvantage of this dyeing method and its utilization of the milling effect is, first,
20 that the drive motors do not pull the dyeing drums through, since there is no weight-distributing dyeing float. A further disadvantage arises in the dyeing of lightweight skins and furs, but also in the case of belly parts of cattlehides, which, without float,
25 frequently curl up too much in the dyeing operation and, as a result, are dyed unevenly. In addition, novel dyeing machines with sieve drums cannot operate the process of cold dyeing without float, since the sieve drum rotates within the dyeing trough and needs a
30 certain level of liquid to immerse therein.

The present invention has for its object to develop a process for dyeing leather which - practised in a one-stage/one-bath dyeing operation with known bottom
35 dyestuffs - provides deep, good leveling and bright dyeings on leather without worsening the fastness values of the dyeings.

It has now been found that, surprisingly, leather can be dyed simultaneously with basic and acidic dyestuffs together in aqueous floats without the occurrence of mutual precipitations of the oppositely charged
5 dyestuffs by using solutions of combinations of these dyestuffs in the presence of alkalis and conducting these dyeings at above pH 7.5 and preferably at between pH 8 and pH 10.

10 Surprisingly, at these pH values, the dyeings in the claimed process can also be effected with heating.

The present invention achieves the stated object primarily on the main leather species most frequently
15 encountered in commercial practice, viz., all chrome- and mineral-tanned leathers. In the case of vegetable-tanned leathers, brightness is good, but depth of shade does not achieve the high values as on chrome leathers.

20 The advantage of the novel process over the dyeing of leather with a single group (acidic or basic) of dyestuffs from hot aqueous floats resides in more saturated and brighter hues and improved fastnesses (light-, water-, wash- and perspiration fastness). Even
25 water-soluble sulfur dyestuffs, which are known to produce but very thin and dull dyeings on leather, produce bright and full hues when applied by the dyeing technique of the present invention.

30 Compared with the sandwich process and the cross-dyeing method involving a change from acidic to basic or from basic to acidic, respectively, the novel process only requires one operation versus 2-3 operations with the
aforementioned types of known dyeing processes, and
35 therefore offers the advantage of being significantly simpler and more time-saving.

Compared with the simultaneous application of cationic and anionic dyestuffs by the process of cold dyeing

without float, the novel dyeing process has the advantage that it can be carried out in any known dyeing apparatus, that the leathers do not entangle and dye more evenly, and more saturated and brighter shades
5 can be achieved.

The process of the present invention can also utilize the known dyeing auxiliaries and fatstuffs, provided they are alkali stable, at the same time in the dyeing,
10 examples being naphthalenesulfonic-aldehyde condensation products, sulfonated fish oils, synthetic fatliquors.

The bronzing of the leather surface frequently observed
15 when comparatively large amounts of basic dyestuffs are used is likewise prevented by the novel dyeing process.

Example 1

Commercially available, chrome-tanned split leather is wetted back in a conventional manner with 600% (based
5 on the dry weight of the leather) of water at 60°C and 2% of ammonia (25% strength) and then dyed in a fresh bath with 600% of an aqueous float according to the five different dyeing methods mentioned hereinbelow:

10 Method 1a

The substrate is dyed in this aqueous float at 60°C with a mixture of

15 1% of sodium carbonate
 5% of the dyestuff Acid Brown 268 and
 3% of the dyestuff Basic Brown 1 - C.I. No. 21000.

After a dyeing time of 45 minutes, the bath has added
20 to it, for fatliquoring,

 3% of a water-soluble anionic fatstuff based on a
 mixture of chloroparaffins and sulfonyl
 chloride

25 and, following treatment under these conditions for a further 15 minutes, the leather is soured off with 6% of formic acid (85% strength).

30 Method 1b

Method 1a is repeated but with the sole use of

 8% of the dyestuff Acid Brown 268.

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Method 1c

The leather article is anionically pre-dyed with

5% of the dyestuff Acid Brown 268

similarly to method 1a or 1b. This is followed by a
cationic after-dyeing of the dyed material in a fresh
5 bath with 600% of aqueous float comprising

3% of the dyestuff Basic Brown 1 - C.I. No. 21000,
dissolved in 3% of formic acid (85% strength). The
10 duration of the after-dyeing is 20 minutes.

Method 1d

The first step comprises performing the dyeing
15 according to method 1a with

4% of the dyestuff Acid Brown 268,

which is followed, after a similar treatment for
20 fatliquoring and after the normal souring off, by a
cationic inter-dyeing of the leather with

3% of the dyestuff Basic Brown 1 - C.I. No. 21000
25 for 20 minutes. Thereafter, the bath is changed and the
substrate is subjected, in a fresh aqueous float, to an
anionic after-dyeing with

1% of the dyestuff Acid Brown 268.
30

Method 1e

The dyeing is performed floatless at room temperature
with a pulverulent mixture of
35

5% of the dyestuff Acid Brown 268 and
3% of the dyestuff Basic Brown 1 - C.I. No. 21000

by milling the leather article for 45 minutes. This is followed by the addition of

5 3% of a water-soluble, anionic fatstuff based on a
 mixture of chloroparaffins and sulfonyl
 chloride

(in the undiluted state), the leather is further
treated under these conditions for 30 minutes and then
10 soured off with 6% of formic acid (85% strength) in the
 course of 15 minutes.

All the leathers dyed according to methods 1a to 1e
were finally rinsed with water in a conventional manner
15 and, after drying, subjected to comparative analysis.

The tabulated compilations which follow provide an
overview of the differences between the modes of
operation according to methods 1a - 1e and also an
20 assessment of the fastness properties achieved in
 accordance with the respective dyeing techniques on the
 dyeings thus produced:

re example 1	No. 1a	1b	1c	1d	1e
method	claimed process	acid dyestuff	acidic/basic	sandwich	cold dyeing w/o float
dyeing at 60°C, % float	600%	600%	600%	600%	-
dyeing at 20°C, no float	-	-	-	-	0%
sodium carbonate	1%	-	-	-	-
Acid Brown 268 (acid dyestuff)	5%	8%	5%	4%	5%
Basic Brown 1 (bas. dyestuff)	3%	-	-	-	3%
anionic fatstuff,					45 min of milling
water soluble	3%	3%	3%	3%	3%
formic acid 85% strength	6%	6%	3%	2%	6%
					20 min of milling
Dyeing operation completed	+	+	-	-	+
Basic Brown 1	/	/	-	3%	/
formic acid 85% strength	/	/	-	3%	/
fresh bath water 60°C	/	/	600%	600%	/
Basic Brown 1	/	/	3%	-	/
Acid Brown 268	/	/	-	1%	/
formic acid 85% strength	/	/	3%	1%	/
					20 min of milling

Fastness values re example 1

Leather No.	Method	1a	1b	1c	1d	1e
depth of shade		9	9	7	9	8
brightness		8	5	7	8	7
penetration		8	5	5	6	6
lightfastness (20 h Fadeometer)		5	5	5	5	5
perspirationfastness (JUF 426)						
to						
a) on cotton		3	1	1	3	3
b) on wool		2	1	1	3	2
Waterfastness (JUF 421)						
to						
a) on cotton		4	4	3	3-4	4
b) on wool		4	3	3	3	
Rubfastness						
Veslic tester (felt staining)						
a) wet rubfastness		3	4	2	1	3
b) dry rubfastness		3-4	4	3-4	2	3-4

5 The brighter and fuller dyeing of leather 1a, dyed by
the novel dyeing process, over leathers 1b (acid
dyeing), 1c (acid dyeing + cationic top dyeing) and 1e
(cold dyeing without float) dyed at equal concentration
is clearly apparent. In terms of brightness, 1a even
10 betters the 1d leather dyed by the cumbersome and risky
sandwich process, whereas the depth of shade of the two
leather dyeings here is about the same.

15 Despite this high depth of shade and brightness, the
through-dyeing of the 1a leather dyed by the novel
method is not reduced compared with the existing dyeing
methods 1b - 1e, as is apparent from a section of a

leather sample. As expected, in terms of dyestuff penetration, the leathers dyed by the top dyeing and sandwich methods (1c and 1d) here give the worst results. In terms of lightfastness, the 5 dyeings are similar.

In the waterfastness and alkaline perspirationfastness tests, the 1a leathers dyed by the novel process exhibit the best fastness values.

The rubfastnesses of all leathers topped with basic dyestuffs are known to be at all times lower than purely acid dyestuff dyeings. Nonetheless, the rubfastness values attainable via the novel process are better than those of the existing method of combination dyeings, albeit without achieving the high values of the purely acid dyestuff dyeing.

Example 2

Split suede leather is wetted back under commercial processing conditions and, for comparative purposes, is dyed, in each case at 60°C, with 600% (on weight of leather) of an aqueous float comprising

- a) 4% of acid dyestuffs
- b) 4% of basic dyestuffs
- c) a mixture of 3% of acid dyestuff and 1% of basic dyestuff in the presence of 2% of sodium carbonate,

in a conventional manner.

The tables which follow specify the individual dyestuffs used therein, followed by an overview of the fastness values of the leather dyeings thus produced:

Assessment re example 2

Leather No.	Depth of shade	Bright- ness	Pene- tra- tion	Light- fast- ness	<u>Rubfast-</u> <u>ness</u>	
					Dry	wet
1a (acidic)	4	5	3	4	4	3
1b (bas.)	1	1	8	3	5	3
1c (acidic/bas./ alk.)	5	7	3	5	4	4
2a	5	5	3	2	4	2-3
2b	2	1	10	1	1	2
2c	6	8	6	3	3-4	3-4
3a	6	5	4	2	3	1
3b	4	1	8	3	2	1
3c	8	7	5	3-4	3	1
4a	6	3	3	3	3	3-4
4b	3	2	10	1	3	1
4c	8	6	5	3-4	3	2-3
5a	3	4	4	3	2-3	1
5b	9	4	7	1	3	0-1
5c	10	6	6	3-4	3	3
6a	4	5	6	1	3-4	3
6b	3	2	9	1	3	0-1
6c	6	6	5	3	3	3

- 5 The comparative leathers dyed up to the same concentration, when compared with the dyeings with the individual dyestuffs, illustrate the increased brightness of the leathers according to group c. These, unlike the dyeing with the individual components: acid

dyestuff (group a) or basic dyestuff (group b), are produced with mixtures of these two oppositely charged dyestuff groups in the same bath in the presence of alkali as per the claimed process. Even combination-
5 shade green dyeings due to mixing acidic and basic blue and yellow brands, i.e., 4-way combinations, are readily obtained using this novel dyeing process (No. 6c).

10 Again, as in example 1, lightfastness is found to be improved over the dyeings with the parent dyestuffs. The wet and dry rubfastnesses of the novel combination method exceed those of the purely basic dyeing and almost achieve the values of the purely acid dyeing.

15

Example 3

Chrome split suede leather in a dyeing drum is wetted back in a customary manner and then dyed in 600% (based
20 on leather dry weight) of an aqueous float for 1 hour at 60°C with

Dyeing 3a

25 a mixture of
5% of the water-soluble acidic sulfur black dyestuff Solubilized Sulphur Black 1 - C.I. No. 53186,
3% of the dyestuff Basic Brown 1 - C.I. No. 21000
30 and
2% of sodium carbonate.

For comparison, two acid dark brown brands frequently encountered in leather factories are
35 dyed up as well, although in this case the quantity used of these acid dyestuffs is actually increased by 2%:

Dyeing 3b

10% of the unitary dark brown dyestuff Acid Brown 268,

5 Dyeing 3c

10% of a mixture of acid dyestuffs which consists of 4 components (brown, blue, yellow, orange).

10

After a dyeing time of 1 hour, the leather is soured off with 5% of formic acid (85% strength) in a customary manner and then further milled for 15 minutes for fixation. After drying, dyeing 3a displays a full and brilliant dark brown which distinctly exceeds the 3b and 3c dyeings with the two acid brown brands.

15

The table which follows gives information about numerical fastness values:

Assessment re example 3

Leather No.	Depth of shade	Bright- ness	Pene- tration	FASTNESSES					Perspi- ration	Dry cleaning
				Light	20 h test	40 h	Co	W	Co	W
3a (acidic/bas./alk.)	10	9	8	5	5	3	4	3	3	5
3b (unitary acid dark brown)	8	5	9	5	4	5	3	1	2	2
3c (dark brown mixed dyestuff)	2	3	9	5	4	4	0-1	0-1	1	140

scale

Staining of
perchloro-
ethylene on
iodine

Dark brown acid dyestuffs with high brightness on leather are not available on the market. Therefore, the dyeing with acid dyestuffs is followed, particularly in the case of suede leather, by a basic top dyeing in a
5 fresh bath.

The novel process makes it possible to increase the brightness of the leather in a very much simpler manner.

10

By admixing the basic medium brown Basic Brown 1 and sodium carbonate it is possible to convert even the extremely dull-dyeing water-soluble sulfur black dyestuff Solubilized Sulphur Black 1 into a brilliant
15 dark brown dyestuff which betters the dark brown single and mixed dyestuffs dyed up in the concurrent test, in terms of brightness and depth of shade, even though it was applied at 20% pure dyestuff less than the acid dyestuffs.

20

Despite the use of the dyestuff Basic Brown 1, which has a relatively poor lightfastness (lightfastness 2), the lightfastness of dyeing 3a at grade 5, even in the 40 hour Fadeometer test, is higher than that of the two
25 acid dyestuff shades 3b and 3c.

Similarly, perspiration resistance is distinctly better for the claimed mixture according to 3a, and in the resistance to dry cleaning, dyeing 3a almost equals the
30 known high fastness values of unitary acid dyestuffs.